



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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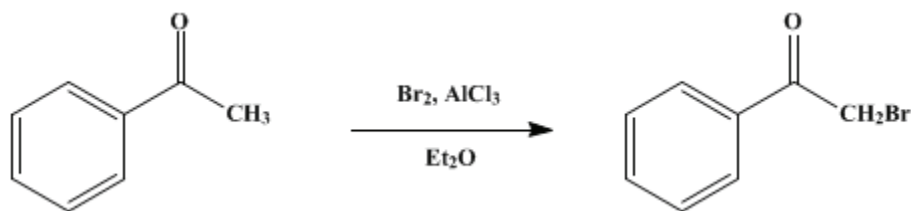
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

PHENACYL BROMIDE

[Acetophenone, α -bromo-]



Submitted by R. M. Cowper and L. H. Davidson.

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1. Procedure

A solution of 50 g. (0.42 mole) of acetophenone (Org. Syn. Coll. Vol. I, 1941, 111) in 50 cc. of pure anhydrous ether (Note 1) is placed in a dry three-necked flask fitted with a separatory funnel, mechanical stirrer, and reflux condenser (Note 2). The solution is cooled in an ice bath, 0.5 g. of anhydrous aluminum chloride is introduced (Note 3), and 67 g. (21.5 cc., 0.42 mole) of bromine is added gradually from the separatory funnel, with stirring, at the rate of about 1 cc. per minute. The bromine color disappears rapidly although very little hydrogen bromide is evolved; towards the end of the reaction the solution becomes pink.

After the bromine has been added the ether and dissolved hydrogen bromide are removed at once (Note 4) under reduced pressure with a slight current of air. The phenacyl bromide remains as a solid mass of brownish yellow crystals (Note 5); the color is removed by shaking with a mixture of 10 cc. of water and 10 cc. of petroleum ether. The crystals are filtered with suction and washed several times with fresh portions of the solvent mixture, if necessary, until a white product is obtained (Note 6). The crude phenacyl bromide weighs 74–80 g. (88–96 per cent of the theoretical amount) and melts at 45–48°. This material is sufficiently pure for many purposes. If higher purity is desired the crude product may be recrystallized from 25–30 cc. of methanol, yielding 54–55 g. (64–66 per cent of the theoretical amount) of white crystals melting at 49–51° (Note 7).

2. Notes

1. Dry carbon tetrachloride may be used as a solvent but is less favorable than dry ether.
2. Quantities up to 200 g. of acetophenone may be brominated in a single operation with equally good yields but this is not generally advisable unless the product is to be used at once, since it becomes discolored on standing.
3. Without aluminum chloride the reaction is slow and incomplete.
4. If the ether and hydrogen bromide are not removed immediately the solution blackens on standing and a lower yield of less pure product results.
5. Phenacyl bromide is a lachrymator and should be manipulated carefully, to avoid contact with the skin and inhalation of the vapor.
6. The water removes yellow color due to residual hydrogen bromide, and the petroleum ether removes unchanged acetophenone or oily by-product. Since the product is quite insoluble in water and only slightly soluble in cold petroleum ether, it may be washed several times with little loss.
7. The checkers observed that all specimens of the product, even after recrystallization, although white at first, became dark and discolored on standing in a vacuum desiccator over calcium chloride.

3. Discussion

Phenacyl bromide has been prepared by the bromination of acetophenone without a solvent,¹ in carbon disulfide,^{2, 3} in acetic acid,^{3, 4, 5} and in other organic solvents.⁵ The quantitative aspects of the

bromination in various solvents have been investigated by Kröhnke.³ The use of ether in the method described is based on the use of this solvent in the bromination of desoxybenzoin.⁶

Phenacyl bromide is a useful reagent for the identification of organic acids by conversion to crystalline phenacyl esters.^{4, 7}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 117](#)

References and Notes

1. Emmerling and Engler, *Ber.* **4**, 148 (1871).
 2. Hunnius, *ibid.* **10**, 2007 (1877); Staedel and Kleinschmidt, *ibid.* **13**, 837 (1880); Staedel, *ibid.* **16**, 22 (1883).
 3. Kröhnke, *ibid.* **69**, 921 (1936).
 4. Rather and Reid, *J. Am. Chem. Soc.* **41**, 77 (1919).
 5. Möhlau, *Ber.* **15**, 2465 (1882); Lazennec, *Bull. soc. chim.* (4) **5**, 501 (1909).
 6. Limpricht and Schwanert, *Ann.* **155**, 68 (1870).
 7. Shriner and Fuson, "The Systematic Identification of Organic Compounds," pp 130 and 132, John Wiley & Sons, New York, 2nd Ed., 1940.
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Desoxybenzoin

petroleum ether

[calcium chloride](#) (10043-52-4)

[acetic acid](#) (64-19-7)

[methanol](#) (67-56-1)

[ether](#) (60-29-7)

[hydrogen bromide](#) (10035-10-6)

[bromine](#) (7726-95-6)

[carbon tetrachloride](#) (56-23-5)

[Acetophenone](#) (98-86-2)

[aluminum chloride](#) (3495-54-3)

[carbon disulfide](#) (75-15-0)

Phenacyl bromide,
Acetophenone, α -bromo- (70-11-1)

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